Preparation of IGZO Thin Layer by a Low-temperature Non-vacuum Technique

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Abstract

Indium-gallium-zinc oxide (IGZO) spherical nanoparticles were obtained by a rapid solvothermal method. Crystal structure of nanoparticles was controlled to obtain homogeneous InGaZnO₄ by tuning of coordination environment of metal ions using diethylene glycol. A low-temperature non-vacuum method to obtain IGZO thin layer is demonstrated by spin coating of our IGZO nanoparticles on SiO₂/Si substrate.

1. Introduction

Recently, In-Ga-Zn-oxide (IGZO) ternary metal oxide thin films received much attention in the field of thin film transistors due to their excellent properties such as high electron mobility (10 cm²/Vs) and wide band gap energy (3.1 eV) [1,2]. Deposition of IGZO thin films are usually carried out by sputtering techniques which require high vacuum conditions. In the case of industrial fabrication of thin films by sputtering techniques, vacuum pumps are responsible for 22% of the total electricity consumption of a factory. Therefore, development of non-vacuum techniques to obtain IGZO thin films is of quite importance to decrease the fabrication cost and environmental load. To this end, previously we reported a mist CVD technique to deposit IGZO channel layer of thin films transistors [3]. IGZO thin film deposition by mist CVD technique required high reaction temperature in the range of 300–450 °C.

On the other hand, flexible electronic devices are currently receiving much attention due to their fascinating features such as foldable displays, bendable solar cells, and wearable sensors [4]. However, the flexible substrates, for example, such as polyethylene tetraphthalate (PET), and polyethylene naphthale (PEN) cannot withstand high reaction temperatures used in mist CVD technique. Therefore, it is important to develop low-temperature non-vacuum processes leading to low-cost flexible electronic devices. To this end, we developed a simple low-temperature chemical process to afford a uniform thin IGZO layer by spin coating of solvothermally prepared spherical IGZO nanoparticles.

In this research, we developed a rapid solvothermal method to afford IGZO spherical fine nanoparticles within 10 min. Homogeneously mixed IGZO spherical nanoparticles with the average size of 100 nm were obtained through rationally designed chemical reactions. Given the importance of the development of low-temperature non-vacuum techniques to obtain thin film transistors, preparation of IGZO thin layer by spin coating of solvothermally prepared spherical nanoparticles is reported in this paper.

2. Experimental Section

Precursor solutions were prepared by dissolving 0.03 mmol of In(NO₃)₃·xH₂O, 0.03 mmol of Ga(NO₃)₃·xH₂O, and 0.03 mmol of Zn(NO₃)₂·6H₂O in 3.5 mL of methanol. The precursor solution was transferred to a 10 mL-capacity SUS-316 stainless steel tubular reactor. The reactor was sealed with a screw cap, placed in a molten salt bath maintained at 300 °C for 10 min period. The reaction was quenched by placing the reactor in an ice-water bath. The resulting powdery products were centrifuged at 6600 rpm for 30 minutes, washed with methanol three times, and dried in vacuum. The procedure was repeated using similar precursor solution with 11.1 mmol of diethylene glycol (DEG). X-ray diffraction (XRD) patterns of the sample were obtained using a Rigaku SmartLab diffractometer with graphite-monochromated Cu Kα radiation. Transmission electron microscope (TEM) images were measured by a JEOL JEM–2100F microscope. Energy dispersive X-ray (EDX) mapping images were obtained from an Oxford INCA energy TEM250. Field emission scanning electron microscope (FESEM) images were obtained by JEOL JSM-7100 microscope. UV-Vis absorption spectra (diffusion reflectance method) were obtained by JASCO UV-650 spectrophotometer equipped with an ISV-722 integration sphere.

IGZO ink was prepared by dispersing 20 mg of IGZO nanoparticles in 4 mL of a mixture of 1:1 (v/v) MeOH and diethylene glycol. A portion of 200 μL of the IGZO ink was spin coated on thermally oxidized SiO₂/Si substrate at 500 rpm for 30 sec. The spin coated substrate was overnight dried in vacuum at room temperature.

3. Results and Discussion

Upon the treatment of precursor solutions containing In(NO₃)₃, Ga(NO₃)₃, and Zn(NO₃)₂ in methanol at 300 °C for 10 min, a white color powdery product was obtained (Fig. 1a). In the STEM/EDX analysis, IGZO yolk-shell nanoparticles are observed. XRD patterns of the sample showed a mixed profile corresponding to amorphous InGaZnO₄ and wurtzite ZnO, indicating that formation of ZnO domains in InGaZnO₄. The formation of ZnO domains

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IGZO nanoparticles through the tuning of coordination environment of In$^{3+}$, Ga$^{3+}$, and Zn$^{2+}$ ions. DEG was chosen as a suitable coordination ligand due to its ability to form coordination complexes with many metal ions, non-toxicity, high thermal stability, and high boiling point. The solvothermal reaction was repeated with 3.5 mL of precursor solution and 1.05 mL (11.1 mmol) of DEG.

Upon the treatment of In(NO$_3$)$_3$·xH$_2$O, Ga(NO$_3$)$_3$·xH$_2$O, and Zn(NO$_3$)$_2$·6H$_2$O and DEG in methanol, similar white color powdery product was obtained. In the STEM/EDX analysis, solid spherical nanoparticles with average size of 100 nm are observed. Moreover, EDX analysis showed that the ratio of In:Ga:Zn is 1:1:1, indicating a strong dependence of atomic ratio of nanoparticles on molar ratio of metal salts in the precursor solutions. XRD patterns showed broad profile corresponding only to amorphous InGaZnO$_4$. Therefore, homogeneously mixed IGZO nanoparticles containing InGaZnO$_4$ were obtained through the tuning the coordination environment of metal ions by suitable ligands. UV-visible absorption spectra of the homogeneously mixed IGZO nanoparticles were measured by diffusion reflectance method and the band gap energy was calculated by Tauc plot method. The calculated band gap energy was 3.1 eV, indicating the high quality of our IGZO nanoparticles. Interestingly, high temperature calcination was not necessary to obtain high quality IGZO nanoparticles by our method.

Our IGZO nanoparticles were dispersed in a mixture of 1:1 (v/v) MeOH and diethylene glycol to prepare IGZO ink. Uniform IGZO thin layer was obtained by spin coating of IGZO ink on SiO$_2$/Si substrate. In near future, our technique will be utilized to the fabrication of flexible electronic devices.

3. Conclusions

A rapid simple solvothermal method was developed to obtain homogeneously mixed IGZO solid spherical nanoparticles by tuning the coordination environments of metal ions. XRD analysis indicated that those IGZO spherical nanoparticles are consisting of InGaZnO$_4$. The band gap energy of IGZO spherical nanoparticles was 3.1 eV. Uniform thin layer of IGZO was obtained by spin coating of our IGZO nanoparticles. Thus, we have demonstrated low-temperature non vacuum method to obtain IGZO thin films.

References